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A model calculation of Raman scattering for resonance excitation to the region of a triplet state

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Abstract : The contributions from the triplet states to vibrational Raman scattering have been discussed and a calculation, based on the parameters of quinoxaline, is presented for understanding the effect of a low lying triplet state on the preresonance Raman excitation profiles of several totally symmetric vibrations. The calculations predict that the triplet state contribution will depend on the linewidths of the triplet state vibrations. In this connection the contributions from some low lying allowed electronic states and their interference effects have also been taken into consideration.

Keywords : Vibronic coupling, spin orbit interaction, Raman excitation profiles

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1. Introduction

Vibronic coupling is a very effective mechanism for mixing two electronic states and thereby making an otherwise forbidden electronic transition allowed by borrowing intensities [1] from nearby suitable allowed electronic transitions. Albrecht used this mechanism and pioneered theoretical work [2] on vibrational Raman spectroscopy. He showed that there are three terms (namely A, B and C) which contribute to Raman scattering. Of these, the A-term is a zero order term which is responsible for enhancing totally symmetric vibrations for tuning the excitation to the resonance region of an allowed electronic transition. The validity of the other two terms has been verified in several cases [3–11]. In Albrecht formulation forbidden electronic states generally do not contribute to Raman intensities except in some special cases where the contribution from the C-term becomes important due to presence of suitable low lying states. But in the last two decades several experimental evidences have been found which indicate that in some cases forbidden electronic states do contribute significantly. Stein *et al* [12]

found antiresonance of some totally symmetric modes of transition metal complex ion for resonance excitation to the absorption maximum of a Laporte forbidden transition. Zgiersky [13] interpreted this phenomenon in terms of second order perturbation theory. Korenowsky *et al* [14] reformulated this theory and applied it do the ν_1 mode of benzene molecule. They predicted a resonance or antiresonance effect for this mode for excitation in resonance with the symmetry forbidden electronic transition $^1B_{2u} \leftarrow {}^1A_{1g}$ which got support from the experiment of Asher and Johnson [15]. Henneker *et al*, using numerical approach and nonadiabatic term [16,17] obtained theoretical excitation profiles. They also considered a system [17] where vibronically coupled allowed and forbidden electronic states exist. Okamoto and co-workers [18] included the contribution of forbidden electronic state for explaining the experimentally observed Raman excitation profiles of tetradesmethyl-β-carotine aggregate even when the excitation is tuned to the allowed electronic transition. Ito *et al* [19] and Hirakawa and Tsuboi [20] discussed the contributions of forbidden transitions from preresonance Raman experiment. Okamoto [21,22] showed that forbidden electronic states may contribute to Raman intensities through second order terms. Several works on enhancement of combination and overtone bands in the Raman spectra have been done for excitation to the region of forbidden electronic transition. Aramaki and co-workers [23] reported a detailed analysis of the fundamental, overtone and combination Raman intensities of the a_{2g} modes of copper tetraphenyl porphyrin. Ohta and Ito [24] and Ziegler and Hudson [25,26] studied the overtones and combinations of ν_6, ν_8 and ν_9 of benzene.

In 1971, Rimai *et al* [27] found peaks in the Raman excitation profiles of vitamin-A (trans-retinal, trans-retinol) and Napthalene at positions where no peaks were obtained in the respective electronic absorption spectra. They showed very convincingly that these peaks correspond to the $S_0 \rightarrow T_1$ transition in the respective molecules. Same kind of observations was also observed in retinylidene Schiff base [28]. In the present paper, we have introduced the contributions from the triplet states to Raman intensities within the frame work of damped Kramers-Heisenberg-Dirac (KHD) formula using spin-orbit mixing of state vectors in the Crude Born Oppenheimer (CBO) adiabatic basis set and made a model calculation for Raman excitation profiles (REP) in order to understand the phenomena of resonance scattering in the vibrational manifold of a triplet state.

2. Theory

To describe vibrational Raman effect, a crude adiabatic Born-Oppenheimer (C B O) basis set is introduced as a zero order state.

The total state vector

$$|S.s\rangle \equiv |S\rangle.|s\rangle, \tag{1}$$

where the capital letter denotes the electronic part and the small letter corresponds to a vibrational level of the respective electronic state. Remember that the electronic state vector

$|S\rangle$ is a CBO state *i.e.* this wave function corresponds to equilibrium configuration. With this basis set the scattering tensor for a Raman transition from an initial vibrational level $|u\rangle$ to a final level $|v\rangle$ of the ground electronic state $|G\rangle$ becomes [29].

$$\left(\alpha_{\rho\sigma}\right)_{GuGv} = (1/h)\sum_{I}\sum_{i}\left[\frac{\langle v|\left(M_{\rho}\right)_{GI}|i\rangle\langle i|\left(M_{\sigma}\right)_{IG}|u\rangle}{\nu_{IiGu}-\nu_{0}-i\tau_{I_i}}\right.$$

$$\left.+\frac{\langle v|\left(M_{\sigma}\right)_{GI}|i\rangle\langle i|\left(M_{\rho}\right)_{IG}|u\rangle}{\nu_{IiGv}+\nu_{0}-i\tau_{I_i}}\right]. \tag{2}$$

Here, $\left(M_{\rho}\right)_{GI} = \langle G|M_{\rho}|I\rangle$ is the ρ-th component of the transition dipole matrix. τ_{I_i} is the linewidth of the state $|Ii\rangle$ and for simplicity the linewidths of the initial $(|Gu\rangle)$ and the final $(|Gv\rangle)$ levels have not been included. For resonance and near resonance excitation $(|Gu\rangle \rightarrow |Ii\rangle)$, the first term in the square bracket is most effective. The contribution from the second term becomes significant for non-resonant excitation.

Let us now consider the case for which the excitation is in resonance or near-resonance with a triplet state $|T\rangle$. For most molecular systems, the ground electronic state is a singlet state. Singlet-triplet transition is forbidden in the Zeroeth order but becomes allowed in the higher order due to mixing of singlet and triplet states through spin-orbit interaction [30]. Thus, the transition moment $(M)_{GT}$ becomes

$$(M)_{GT} = \langle G|M|T\rangle \cong \sum_{S\neq T}\frac{\langle S|H_{SO}|T\rangle}{E_T - E_S}\cdot(M)_{GS}, \tag{3}$$

where $|S\rangle$ is an allowed singlet state and the spin orbit interaction Hamiltonian H_{SO} is given by [30]

$$H_{SO} = \frac{e^2}{2m^2c^2}\sum_{k}\sum_{i}\frac{Z_k}{r_{ki}^3}\,l_i\cdot S_i, \tag{4}$$

where l_i and S_i are respectively the orbital and spin angular momentum operators of the i-th electron at a distance r_{ki} from the k-th nucleus with atomic number Z_k. In eq. (3) we have neglected the mixing of the ground electronic state $|G\rangle$ with others.

Thus, the contribution of A-term [31] to the polarizability tensor for resonance or near resonance excitation becomes

$$A \cong \frac{1}{h}\sum_{t}\frac{1}{\nu_{TtGu}-\nu_{0}-i\tau_{Tt}}\sum_{S\neq T,\,S'}\sum\frac{\langle S|H_{SO}|T\rangle\langle T|H_{SO}|S'\rangle}{\left(E_T-E_S\right)\left(E_T-E_{S'}\right)}$$

$$\times\left(M_{\rho}\right)_{GS}\left(M_{\sigma}\right)_{S'G}\langle v|t\rangle\langle t|u\rangle \tag{5}$$

Here, all the small letters are the vibrational levels of the corresponding electronic states denoted by capital letters. Eq. (5) indicates that the scattering tensor becomes appreciable if and only if the resonating triplet state $|T\rangle$ has at least one nearby allowed singlet state with sufficiently large spin-orbit interaction between them. But under such condition the preresonance contribution from the nearby allowed singlet state becomes important. For resonant excitation in the region of such a triplet state, the resonance and preresonance contributions may be compared from eqs. (2) and (5). For preresonance contribution only the A-term from the resonant part (first term in the square bracket of eq. (2)) is considered. Thus, we get

$$\left|\frac{\alpha_{\text{Res}}}{\alpha_{\text{Pre Res}}}\right| \cong \left[\frac{\langle H_{SO}\rangle}{E_T - E_S}\right]^2 \cdot \left|\frac{\nu_{S_1G_0} - \nu_0 - i\tau_{S_1}}{i\tau_{T_1}}\right| \tag{6}$$

For aromatic heterocyclic (oxygen and nitrogen) and carbonyl molecules [30,32] $\langle H_{SO}\rangle \cong 10\ \text{cm}^{-1}$, $\nu_{S_1G_0} - \nu_0 - i\tau_{S_1} \cong E_S - E_T \cong 1000\ \text{cm}^{-1}$, then

$$\left|\frac{\alpha_{\text{Res}}}{\alpha_{\text{Pre Res}}}\right| \cong \frac{1}{10\,\tau_{T_1}}. \tag{7}$$

Thus, we see that triplet linewidth plays an important role in determining the magnitude of the resonance contribution. This is expected to be very significant in supercooled supersonic jet molecules. Thus, there is a possibility of finding the triplet states, which are inaccessible by other methods (like electronic absorption or emission spectroscopy), by examining the REP of such molecules.

3. A model calculation and discussion

Excitation frequency dependence of the intensities of different normal vibrations of quinoxaline molecule in Raman scattering was previously studied by Aminzadeh *et al* [33]. In order to test the above ideas, we have used this molecule as a model system and calculated REPs of some totally symmetric vibrations and critically examined the nature of the profiles near the lowest singlet triplet transition.

The low lying electronic states of the molecule are shown in Table 1. The lowest triplet state at 21480 cm^{-1} is a triplet of $\pi\pi^*$-type character [34]. Of the singlet states only the lowest one is an $n\pi^*$-state of symmetry $^1B_1$. Hence this is the only singlet state which can mix significantly with the above triplet state through spin-orbit interaction [35]. The f-values of different $G(=S_0) \rightarrow S_i$ transitions, their directions of polarisation and absolute magnitudes of the transition dipole moments in some arbitrary unit are also shown in Table 1.

Since we are considering only totally symmetric vibrations, only the diagonal elements (α_{xx} and α_{yy}) of the polarizability tensor (See Table 1) will contribute to their Raman intensities. The triplet, $|T\rangle$ and the lowest singlet, $|S_1\rangle$ states will contribute to α_{yy} and the

other singlet states to the α_{xx}-component. The two components are (considering both resonance and off-resonance excitation simultaneously)

Table 1. Particulars about some low energy electronic states of quinoxaline

Electronic states* (symmetries)	Energies . cm^{-1}	f-values of different $G \rightarrow S_t$ transitions with their directions of polarization indicated within the brackets*	Absolute values of the corresponding transition dipole moments in some arbitrary unit[b] M_x	M_z
$G = S_0(^1A_1)$	0			
$T(^3B_2)$	21480			
$S_1(^1B_1)$	27070	0.0174[a] (Calc Z)		0.4000
$S_2(^1A_1)$	32268	0.130 (X)	1.0000	
$S_3(^1A_1)$	43158	0.305 (X)	1.3245	
$S_4(^1A_1)$	51000	0.606 (X)	1.7174	

* [34, 39, 41]

[a] This value is calculated from the data given in the reference [34]

[b] These values are calculated from the formula $^fGS_t = \text{const}\ ^vGS_t \left|^MGS_t\right|^2$

$$(\alpha_{zz})_{GuGu} = (1/h)\left|(M_z)_{GS_1}\right|^2 \left\{ \sum_t \left|\frac{\langle S_1|H_{SO}|T\rangle}{E(T_1)-E(S_1)}\right|^2 \left[\frac{1}{(\nu_{TuGu}-\nu_0-i\tau_{T_t})} + \frac{1}{(\nu_{TuGu}+\nu_0-i\tau_{T_t})}\right]\langle v|t\rangle\langle t|u\rangle + \sum_{s_1}\left[\frac{1}{(\nu_{S_1s_1Gu}-\nu_0-i\tau_{S_1s_1})} + \frac{1}{(\nu_{S_1s_1Gu}+\nu_0-i\tau_{S_1s_1})}\right]\langle v|s_1\rangle\langle s_1|u\rangle\right\} \quad (8a)$$

and

$$(\alpha_{xx})_{GuGu} = \frac{1}{h}\sum_{t=2}^{4}\sum_{s_t}\left|(M_x)_{GS_t}\right|^2 \left[\frac{1}{(\nu_{S_ts_tGu}-\nu_0-i\tau_{S_ts_t})} + \frac{1}{(\nu_{S_ts_tGu}+\nu_0-i\tau_{S_ts_t})}\right]\langle v|s_t\rangle\langle s_t|u\rangle \quad (8b)$$

Here one thing is worthy to mention. Since we have calculated REP over a wide range of excitation frequencies, we wanted to express the intensity by a single formula for both

resonance or near resonance and off-resonance excitation. This is the reason for using both the resonance and the off-resonance parts of the scattering tensor in eqs. 8(a) and 8(b). Using independent mode approximation [36], the multidimensional overlap integral may be reduced to the product of one dimensional integrals. Neglecting the distortion of the excited state potentials, the one dimensional overlap integrals may be obtained from the recurrence relations of Manneback [37]. For small displacement of the excited state potential minima with respect to that of the ground state, it can be shown [38] that (for excitation of the fundamental vibration of the a-th normal mode)

$$\begin{aligned} \langle v|i\rangle\langle i|u\rangle &= \Delta_a^I \quad \text{for } i_a = 0 \\ &= -\Delta_a^I \quad \text{for } i_a = 1 \end{aligned} \tag{9}$$

where i_a is the vibrational quantum number associated with the a-th normal mode in the excited electronic state $|I\rangle$ and Δ_a^I is the displacement of the potential minimum of the excited state $|I\rangle$ with respect to that the ground state along the a-th normal mode of vibration. Thus, eqs. 8(a) and 8(b) become

$$\begin{aligned} (\alpha_{zz})^a_{G0G1} = \frac{1}{h}\left|(M_z)_{GS_1}\right|^2 \nu_a \Bigg[\Delta_{Ta} \left|\frac{\langle S_1|H_{SO}|T\rangle}{E(T)-E(S_1)}\right|^2 \\ \times\Bigg\{\frac{1}{\left(\nu_{T0G0}-\nu_0-i\tau_T\right)\left(\nu_{T0G0}+\nu_a-\nu_0-i\tau_T\right)} \\ + \frac{1}{\left(\nu_{T0G0}+\nu_0-i\tau_T\right)\left(\nu_{T0G0}-\nu_a+\nu_0-i\tau_T\right)}\Bigg\} \\ + \Delta_{S_1a}\Bigg\{\frac{1}{\left(\nu_{S_10G0}-\nu_0-i\tau_{S_1}\right)\left(\nu_{S0G0}+\nu_a-\nu_0-i\tau_{S_1}\right)} \\ + \frac{1}{\left(\nu_{S_10G0}+\nu_0-i\tau_{S_1}\right)\left(\nu_{S_10G0}-\nu_a+\nu_0-i\tau_{S_1}\right)}\Bigg]. \end{aligned} \tag{10a}$$

$$\begin{aligned} (\alpha_{xx})^a_{G0G1} = \frac{1}{h}\sum_i \left|(M_x)_{GS_i}\right|^2 \nu_a \sum_{i=2}^{4} \Delta_{S_ia} \\ \times\Bigg[\frac{1}{\left(\nu_{S_i0G0}-\nu_0-i\tau_{S_i}\right)\left(\nu_{S_i0G0}+\nu_a-\nu_0-i\tau_{S_i}\right)} \\ + \frac{1}{\left(\nu_{S_i0G0}+\nu_0-i\tau_{S_i}\right)\left(\nu_{S_i0G0}-\nu_a+\nu_0-i\tau_{S_i}\right)}\Bigg] \end{aligned} \tag{10b}$$

Here, we have assumed $\tau_{T0} = \tau_{T1} = \tau_T$ and $\tau_{S,0} = \tau_{S,1} = \tau_S$. Thus, we have calculated Raman intensities in some arbitrary unit *i.e.*

$$I^a_{G0G1} = C(\nu_0 - \nu_a)^4 \left[\left| (\alpha_{xx})^a_{G0G1} \right|^2 + \left| (\alpha_{zz})^a_{G0G1} \right|^2 \right]. \tag{11}$$

In eq. (11), not only the diagonal contributions from individual states but also the interference effects of the contributions from appropriate states have been taken into consideration. Expressions similar to Clark and Dines [36] for the interference terms, appearing from both the resonant and off-resonant part of the scattering tensor, for intensities have been used. Since we have special interest in the region of resonance excitation to the $G \rightarrow T$ transition, the linewidth of triplet state (τ_T) will play some important role whereas the effect of the linewidths of the singlet states are practically negligible. Thus we have calculated REPs of some totally symmetric vibrations of quinoxaline of frequencies 532, 758, 1204, 1367, 1415 and 1570 cm^{-1} for some selective values of the parameters : $<H_{S0}> \equiv 15$ cm^{-1} and $\tau_T = 10$, 1 and 0.1 cm^{-1}. The calculations are shown in Figure 1. For each normal vibration, the intensities are normalized relative to that associated with the excitation frequency ($\nu_0 = 20490$ cm^{-1}). The results are compared with the corresponding observed profiles [33]. The fitting is

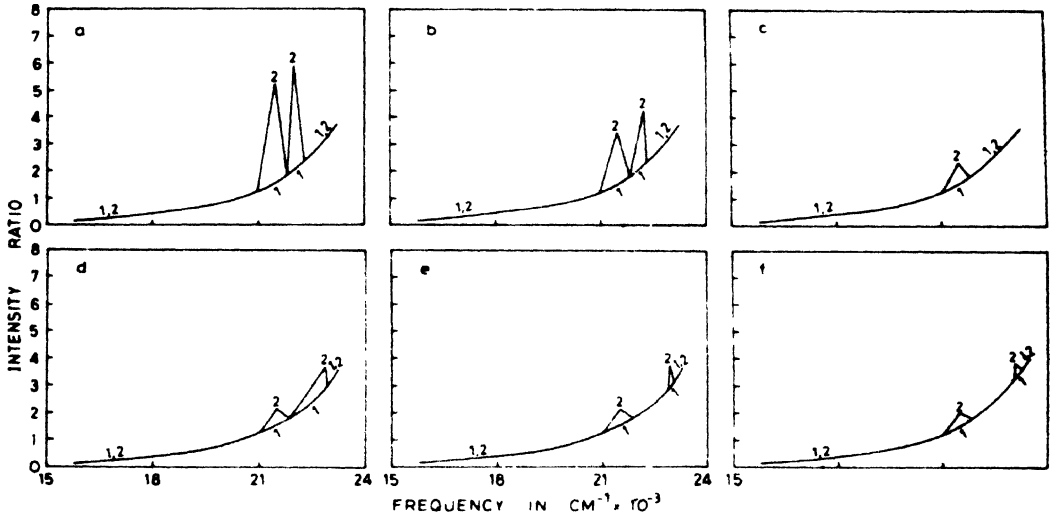

Figure 1. Calculated Raman excitation profiles of some totally symmetric vibrations of quinoxaline a 532 cm^{-1} b 758 cm^{-1}, c 1204 cm^{-1}, d 1367 cm^{-1}, e 1415 cm^{-1} and f 1570 cm^{-1}
[Raman excitation profiles are calculated for $\tau_T = 10$ and 1 cm^{-1} (1) and 0.1 cm^{-1} (2)].

more or less fair. In order to see the effect of triplet state linewidth on the Raman scattering, we have calculated REPs for three values of τ_T mentioned above. They are found to be identical except at exact resonance (*i.e.* at $\nu_0 = \nu_{I0G0}$ and $\nu_{I0G0} + \nu_a$) where resonance enhancement is predominant for the lowest value of $\tau_T = 0.1$ cm^{-1}. This means that

molecules, possessing such order of triplet state linewidth, resonance enhancement in the region of the triplet state may be observed. This possibility was previously pointed out by Mallick [40]. This is expected in supercooled molecules in the supersonic jet.

In this model calculation, we have assumed that the shift of all the excited state potential minima with respect to that of the ground state are equal. This may be one of the reasons of having results not in absolute agreement with observation. Exclusion of the distortion of excited state potential may also yield some error in calculating REPs. Besides these, we have found that contributions from the $|S_1\rangle$ and $|T\rangle$ states interfere significantly only in the resonance or near-resonance excitation to the triplet state $|T\rangle$. This interference is both constructive and destructive depending respectively on the excitations lying beyond and below the resonance. The contributions from the other three singlet states belonging to the symmetry species A_1 interfere constructively significantly (specially $|S_3\rangle$ and $|S_4\rangle$ with $|S_2\rangle$).

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